1

Numbers, Measurements, and Numerical Mathematics

Preview

The first application of mathematics to chemistry deals with various physical quantities that have numerical values. In this chapter, we introduce the correct use of numerical values to represent measured physical quantities and the use of numerical mathematics to calculate values of other quantities. Such values generally consist of a number and a unit of measurement, and both parts of the value must be manipulated correctly. We introduce the use of significant digits to communicate the probable accuracy of the measured value. We also review the factor-label method, which is a routine method of expressing a measured quantity in terms of a different unit of measurement.

Principal Facts and Ideas

1. Specification of a measured quantity consists of a number and a unit.
2. A unit of measurement is an arbitrarily defined quantity that people have agreed to use.
3. The SI units have been officially adopted by international organizations of physicists and chemists.
4. Consistent units must be used in any calculation.
5. The factor-label method can be used to convert from one unit of measurement to another.
6. Reported values of all quantities should be rounded so that insignificant digits are not reported.

Objectives

After you have studied the chapter, you should be able to:

1. use numbers and units correctly to express measured quantities;
2. understand the relationship of uncertainties in measurements to the use of significant digits;
3. use consistent units, especially the SI units, in equations and formulas; and
4. use the factor-label method to convert from one unit of measurement to another.

1.1 Numbers and Measurements

The most common use that chemists make of numbers is to report values for measured quantities. Specification of a measured quantity generally includes a number and a unit of measurement. For example, a length might be given as 12.00 inches (12.00 in) or 30.48 centimeters (30.48 cm), or 0.3048 meters (0.3048 m), and so on. Specification of the quantity is not complete until the unit of measurement is specified. For example, 30.48 cm is definitely not the same as 30.48 in. We discuss numbers in this section of the chapter, and will use some common units of measurement. We discuss units in the next section.

Numbers

There are several sets into which we can classify numbers. The numbers that can represent physical quantities are called *real numbers*. These are the numbers with which we ordinarily deal, and they consist of a magnitude and a sign, which can be positive or negative. Real numbers can range from positive numbers of indefinitely large magnitude to negative numbers of indefinitely large magnitude. Among the real numbers are the *integers* $0, \pm 1, \pm 2, \pm 3$, and so on, which are part of the *rational numbers*. Other rational numbers are quotients of two integers, such as $\frac{2}{3}, \frac{7}{9}, \frac{37}{53}$. Fractions can be represented as decimal numbers. For example, $\frac{1}{16}$ is the same as 0.0625. Some fractions cannot be represented exactly by a decimal number with a finite number of nonzero digits. For example, $\frac{1}{3}$ is represented by $0.333333\cdots$. The three dots (an ellipsis) that follow the given digits indicate that more digits follow. In this case, infinitely many digits are required for an exact representation. However, the decimal representation of a rational number either has a finite number of nonzero digits or contains a repeating pattern of digits.

EXERCISE 1.1 ▶ Take a few simple fractions, such as $\frac{2}{3}$, $\frac{4}{9}$, or $\frac{3}{7}$ and express them as decimal numbers, finding either all of the nonzero digits or the repeating pattern of digits. ◀

The numbers that are not rational numbers are called *irrational numbers*. *Algebraic irrational number* include square roots of rational numbers, cube roots of rational numbers, and so on, which are not themselves rational numbers. All of the rest of the real numbers are called *transcendental irrational numbers*. Two commonly encountered transcendental irrational numbers are the ratio of the circumference of a circle to its diameter, called π and given by $3.141592653\cdots$, and the *base of natural logarithms*, called e and given by $2.718281828\cdots$. Irrational numbers have the property that if you have some means of finding what the correct digits are, you will never reach a point beyond which all of the remaining digits are zero, or beyond which the digits form some other repeating pattern.[1]

In addition to real numbers, mathematicians have defined *imaginary numbers* into existence. The *imaginary unit*, i, is defined to equal $\sqrt{-1}$. An *imaginary number* is equal to a real number times i, and a *complex number* is equal to a real number plus an imaginary number. If x and y are real numbers, then the quantity $z = x + iy$ is a complex number. x is called the *real part* of z, and the real number y is called the *imaginary part* of z. Imaginary and complex numbers cannot represent physically measurable quantities, but turn out to have important applications in quantum mechanics. We will discuss complex numbers in the next chapter.

The numbers that we have been discussing are called *scalars*, to distinguish them from *vectors*. A scalar number has magnitude and sign, and a vector has both magnitude and direction. We will discuss vectors later, and will see that a vector can be represented by several scalars.

Measurements, Accuracy, and Significant Digits

A measured quantity can almost never be known with complete exactness. It is therefore a good idea to communicate the probable accuracy of a reported measurement. For example, assume that you measured the length of a piece of glass tubing with a meter stick and that your measured value was 387.8 millimeters (387.8 mm). You decide that your experimental error was probably no greater than 0.6 mm. The best way to specify the length of the glass tubing is

$$\textit{length} = 387.8\,\text{mm} \pm 0.6\,\text{mm}$$

If for some reason you cannot include a statement of the probable error, you should at least avoid including digits that are probably wrong. In this case, your estimated error is somewhat less than 1 mm, so the correct number is probably closer to 388 mm than to either 387 mm or 389 mm. If we do not want to report the expected experimental error, we report the length as 388 mm and assert that the three digits given are *significant digits*. This means that the given digits are correctly stated. If we had reported the length as 387.8 mm, the last digit is *insignificant*. That is, if we knew the exact length, the digit 8 after the decimal point is probably not the correct digit, since we believe that the correct length lies between 387.2 mm and 388.4 mm.

You should always avoid reporting digits that are not significant. When you carry out calculations involving measured quantities, you should always determine how many significant digits your answer can have and round off your result to that number of digits. When values of physical quantities are given in a physical chemistry textbook or in this book, you can assume that all digits specified are significant. If you are given a number that you believe to be correctly stated, you can count the number of significant digits. If there are no zeros in the number, the number of significant digits is just the number of digits. If the number contains one or more zeros, any zero that occurs between nonzero digits does count as a

[1] It has been said that early in the twentieth century the legislature of the state of Indiana, in an effort to simplify things, passed a resolution that henceforth in that state, π should be exactly equal to 3.

significant digit. Any zeros that are present only to specify the location of a decimal point do not represent significant digits. For example, the number 0.0000345 contains three significant digits, and the number 0.003045 contains four significant digits. The number 76,000 contains only two significant digits. However, the number 0.000034500 contains five significant digits. The zeros at the left are present only to locate the decimal point, but the final two zeros are not needed to locate a decimal point, and therefore must have been included because the number is known with sufficient accuracy that these digits are significant.

A problem arises when zeros that appear to occur only to locate the decimal point are actually significant. For example, if a mass is known to be closer to 3500 grams (3500 g) than to 3499 g or to 3501 g, there are four significant digits. If one simply wrote 3500 g, persons with training in significant digits would assume that the zeros are not significant and that there are two significant digits. Some people communicate the fact that there are four significant digits by writing 3500. grams. The explicit decimal point communicates the fact that the zeros are significant digits. Others put a bar over any zeros that are significant, writing $35\bar{0}\bar{0}$ to indicate that there are four significant digits.

Scientific Notation

The communication difficulty involving significant zeros can be avoided by the use of *scientific notation*, in which a number is expressed as the product of two factors, one of which is a number lying between 1 and 10 and the other is 10 raised to some integer power. The mass mentioned above would thus be written as 3.500×10^3 g. There are clearly four significant digits indicated, since the trailing zeros are not required to locate a decimal point. If the mass were known to only two significant digits, it would be written as 3.5×10^3 g.

Scientific notation is also convenient for extremely small or extremely large numbers. For example, *Avogadro's constant*, the number of molecules or other formula units per mole, is easier to write as 6.02214×10^{23} mol^{-1} than as 602,214,000,000,000,000,000,000 mol^{-1}, and the charge on an electron is easier to write and read as 1.60217×10^{-19} coulomb (1.60217×10^{-19} C) than as 0.000000000000000000160217 C.

EXERCISE 1.2 ▶ Convert the following numbers to scientific notation, using the correct number of significant digits:

(a) 0.000598 (b) 67, 342, 000

(c) 0.000002 (d) 6432.150

◀

Rounding

The process of rounding is straightforward in most cases. The calculated number is simply replaced by that number containing the proper number of digits that is closer to the calculated value than any other number containing this many digits. Thus, if there are three significant digits, 4.567 is rounded to 4.57, and 4.564 is rounded to 4.56. However, if your only insignificant digit is a 5, your calculated number is midway between two rounded numbers, and you must decide whether to round up or to round down. It is best to have a rule that will round down half of the time and round up half of the time. One widely used rule is to round to the even digit, since there is a 50% chance that any digit will be even. For example, 2.5 would be rounded to 2, and 3.5 would be rounded to 4. An equally valid procedure that is apparently not generally used would be to toss a coin and round up if the coin comes up "heads" and to round down if it comes up "tails."

EXERCISE 1.3 ▶ Round the following numbers to four significant digits

(a) 0.2468985 (b) 78955

(c) 123456789 (d) 46.4535

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1.2 Numerical Mathematical Operations

We are frequently required to carry out numerical operations on numbers. The first such operations involve pairs of numbers.

Elementary Arithmetic Operations

The elementary mathematical operations are addition, subtraction, multiplication, and division. Some rules for operating on numbers with sign can be simply stated:

1. The product of two factors of the same sign is positive, and the product of two factors of different signs is negative.
2. The quotient of two factors of the same sign is positive, and the quotient of two factors of different signs is negative.
3. The difference of two numbers is the same as the sum of the first number and the negative of the second.
4. Multiplication is *commutative*, which means that[2] if a and b stand for numbers

$$\boxed{a \times b = b \times a.} \tag{1.1}$$

5. Multiplication is *associative*, which means that

$$\boxed{a \times (b \times c) = (a \times b) \times c.} \tag{1.2}$$

6. Multiplication and addition are *distributive*, which means that

$$\boxed{a \times (b + c) = a \times b + a \times c.} \tag{1.3}$$

[2] We enclose equations that you will likely use frequently in a box.

Additional Mathematical Operations

In addition to the four elementary arithmetic operations, there are some other important mathematical operations, many of which involve only one number. The *magnitude*, or *absolute value*, of a scalar quantity is a number that gives the size of the number irrespective of its sign. It is denoted by placing vertical bars before and after the symbol for the quantity. This operation means

$$|x| = \begin{cases} x & \text{if } x \geq 0 \\ -x & \text{if } x < 0 \end{cases} \tag{1.4}$$

For example,

$$\begin{aligned} |4.5| &= 4.5 \\ |-3| &= 3 \end{aligned}$$

The magnitude of a number is always nonnegative (positive or zero).

Another important set of numerical operations is the taking of *powers and roots*. If x represents some number that is multiplied by itself $n - 1$ times so that there are n factors, we represent this by the symbol x^n, representing x to the nth power. For example,

$$x^2 = x \times x, \quad x^3 = x \times x \times x, \quad x^n = x \times x \times x \times \cdots \times x \quad (n \text{ factors}). \tag{1.5}$$

The number n in the expression x^n is called the *exponent* of x. If the exponent is not an integer, we can still define x^n. We will discuss this when we discuss logarithms. An exponent that is a negative number indicates the reciprocal of the quantity with a positive exponent:

$$\boxed{x^{-1} = \frac{1}{x}, \quad x^{-3} = \frac{1}{x^3}} \tag{1.6}$$

There are some important facts about exponents. The first is

$$\boxed{x^a x^b = x^{a+b}} \tag{1.7}$$

where x, a, and b represent numbers. We call such an equation an *identity*, which means that it is correct for all values of the variables in the equation. The next identity is

$$\boxed{(x^a)^b = x^{ab}} \tag{1.8}$$

Roots of real numbers are defined in an inverse way from powers. For example, the *square root* of x is denoted by $\sqrt{x}$ and is defined as the number that yields x when squared:

$$(\sqrt{x})^2 = x \tag{1.9}$$

The *cube root* of x is denoted by $\sqrt[3]{x}$, and is defined as the number that when cubed (raised to the third power) yields x:

$$\left(\sqrt[3]{x}\right)^3 = x \tag{1.10}$$

Fourth roots, fifth roots, and so on, are defined in similar ways. The operation of taking a root is the same as raising a number to a fractional exponent. For example,

$$\sqrt[3]{x} = x^{1/3} \tag{1.11}$$

This equation means that

$$\left(\sqrt[3]{x}\right)^3 = (x^{1/3})^3 = x = (x^3)^{1/3} = \sqrt[3]{x^3}.$$

This equation illustrates the fact that the order of taking a root and raising to a power can be reversed without changing the result. We say that these operations *commute* with each other.

There are two numbers that when squared will yield a given positive real number. For example, $2^2 = 4$ and $(-2)^2 = 4$. When the symbol $\sqrt{4}$ is used, only the positive square root, 2, is meant. To specify the negative square root of x, we write $-\sqrt{x}$. If we confine ourselves to real numbers, there is no square root, fourth root, sixth root, and so on, of a negative number. In Section 2.6, we define imaginary numbers, which are defined be square roots of negative quantities. Both positive and negative numbers can have real cube roots, fifth roots, and so on, since an odd number of negative factors yields a negative product.

The square roots, cube roots, and so forth, of integers and other rational numbers are either rational numbers or *algebraic irrational numbers*. The square root of 2 is an example of an *algebraic irrational number*. An algebraic irrational number produces a rational number when raised to the proper integral power. When written as a decimal number, an algebraic irrational number does not have a finite number of nonzero digits or exhibit any pattern of repeating digits. An irrational number that does not produce a rational number when raised to any integral power is a *transcendental irrational number*. Examples are e, the base of natural logarithms, and π, the ratio of a circle's circumference to its diameter.

Logarithms

We have discussed the operation of raising a number to an integral power. The expression a^2 means $a \times a$, a^{-2} means $1/a^2$, a^3 means $a \times a \times a$, and so on. In addition, you can have exponents that are not integers. If we write

$$y = a^x \tag{1.12}$$

the exponent x is called the *logarithm of y to the base a* and is denoted by

$$x = \log_a(y) \tag{1.13}$$

If a is positive, only positive numbers possess real logarithms.

Common Logarithms

If the base of logarithms equals 10, the logarithms are called *common logarithms:* If $10^x = y$, then x is the common logarithm of y, denoted by $\log_{10}(y)$. The subscript 10 is sometimes omitted, but this can cause confusion.

For integral values of x, it is easy to generate the following short table of common logarithms:

y	$x = \log_{10}(y)$	y	$x = \log_{10}(y)$
1	0	0.1	-1
10	1	0.01	-2
100	2	0.001	-3
1000	3	*etc.*	

In order to understand logarithms that are not integers, we need to understand exponents that are not integers.

EXAMPLE 1.1 Find the common logarithm of $\sqrt{10}$.

SOLUTION ► The square root of 10 is the number that yields 10 when multiplied by itself:

$$\left(\sqrt{10}\right)^2 = 10.$$

We use the fact about exponents

$$\left(a^x\right)^z = a^{xz}. \tag{1.14}$$

Since 10 is the same thing as 10^1,

$$\sqrt{10} = 10^{1/2}. \tag{1.15}$$

Therefore

$$\log_{10}\left(\sqrt{10}\right) = \log_{10}(3.162277...) = \frac{1}{2} = 0.5000$$

◄

Equation (1.14) and some other relations governing exponents can be used to generate other logarithms, as in the following problem.

EXERCISE 1.4 ► Use Eq. (1.14) and the fact that $10^{-n} = 1/(10^n)$ to generate the negative logarithms in the short table of logarithms. ◄

We will not discuss further how the logarithms of various numbers are computed. Extensive tables of logarithms with up to seven or eight significant digits were once in common use. Most electronic calculators provide values of logarithms with as many as 10 or 11 significant digits. Before the invention of electronic calculators, tables of logarithms were used when a calculation required more significant digits than a slide rule could provide. For example, to multiply two numbers together, one would look up the logarithms of the two numbers, add the logarithms and then look up the *antilogarithm* of the sum (the number possessing the sum as its logarithm).

Natural Logarithms

Besides 10, there is another commonly used base of logarithms. This is a transcendental irrational number called e and equal to 2.7182818...

$$\boxed{\text{If } e^y = x \quad \text{then } y = \log_e(x) = \ln(x).} \tag{1.16}$$

Logarithms to this base are called *natural logarithms*. The definition of e is[3]

$$e = \lim_{n\to\infty}\left(1+\frac{1}{n}\right)^n = 2.7182818\ldots \tag{1.17}$$

The "lim" notation means that larger and larger values of n are taken.

EXERCISE 1.5 ▶ Evaluate the quantity $(1+\frac{1}{n})^n$ for several integral values of n ranging from 1 to $1,000,000$. Notice how the value approaches the value of e as n increases. ◀

The notation $\ln(x)$ is more common than $log_e(x)$. Natural logarithms are also occasionally called *Napierian logarithms*.[4] Unfortunately, some mathematicians use the symbol $\log(y)$ without a subscript for natural logarithms. Chemists frequently use the symbol $\log(y)$ without a subscript for common logarithms and the symbol $\ln(y)$ for natural logarithms. Chemists use both common and natural logarithms, so the best practice is to use $\log_{10}(x)$ for the common logarithm of x and $\ln(x)$ for the natural logarithm of x.

If the common logarithm of a number is known, its natural logarithm can be computed as

$$e^{\ln(y)} = 10^{\log_{10}(y)} = \left(e^{\ln(10)}\right)^{\log_{10}(y)} = e^{\ln(10)\log_{10}(y)}. \tag{1.18}$$

The natural logarithm of 10 is equal to $2.302585\ldots$, so we can write

$$\boxed{\ln(y) = \ln(10)\log_{10}(y) = (2.302585\cdots)\log_{10}(y)}. \tag{1.19}$$

In order to remember Eq. (1.19) correctly, keep the fact in mind that since e is smaller than 10, the natural logarithm is larger than the common logarithm.

EXERCISE 1.6 ▶ Without using a calculator or a table of logarithms, find the following:

(a) $\ln(100.000)$ (b) $\ln(0.0010000)$

(c) $\log_{10}(e)$

◀

Logarithm Identities

There are a number of identities involving logarithms, some of which come from the exponent identities in Eqs. (1.6)–(1.8). Table 1.1 lists some identities involving exponents and logarithms. These identities hold for common logarithms and natural logarithms as well for logarithms to any other base.

[3] The base of natural logarithms, e, is named after Leonhard Euler, 1707–1783, a great Swiss mathematician.

[4] Naperian logarithms are named after John Napier, 1550–1617, a Scottish landowner, theologian, and mathematician, who was one of the inventors of logarithms.

TABLE 1.1 ► Properties of Exponents and Logarithms

Exponent fact	Logarithm fact
$a^0 = 1$	$\log_a(1) = 0$
$a^{1/2} = \sqrt{a}$	$\log_a\left(\sqrt{a}\right) = \frac{1}{2}$
$a^1 = a$	$\log_a(a) = 1$
$a^{x_1}a^{x_2} = a^{x_1+x_2}$	$\log_a(y_1 y_2) = \log_a(y_1) + \log_a(y_2)$
$a^{-x} = \frac{1}{a^x}$	$\log_a\left(\frac{1}{y}\right) = -\log_a(y)$
$\frac{a^{x_1}}{a^{x_2}} = a^{x_1-x_2}$	$\log_a\left(\frac{y_1}{y_2}\right) = \log_a(y_1) - \log_a(y_2)$
$(a^x)^z = a^{xz}$	$\log_a(y^z) = z\log_a(y)$
$a^{\infty} = \infty$	$\log_a(\infty) = \infty$
$a^{-\infty} = 0$	$\log_a(0) = -\infty$

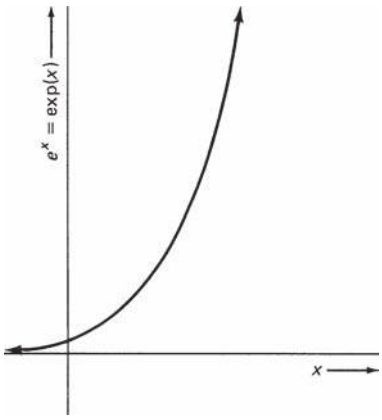

Figure 1.1 ► The exponential function.

The Exponential

The *exponential* is the same as raising e (the base of natural logarithms, equal to $2.7182818284\cdots$) to a given power and is denoted either by the usual notation for a power, or by the notation $\exp(\cdots)$.

$$y = ae^{bx} \equiv a\exp(bx)\,, \tag{1.20}$$

Figure 1.1 shows a graph of this function for $b > 0$.

The graph in Fig. 1.1 exhibits an important behavior of the exponential e^{bx}. For $b > 0$, it doubles each time the independent variable increases by a fixed amount whose value depends on the value of b. For large values of b the exponential function becomes large very rapidly. If $b < 0$, the function decreases to half its value each time the independent variable increases by a fixed amount. For large negative values of b the exponential function becomes small very rapidly.

EXERCISE 1.7 ► For a positive value of b find an expression for the change in x required for the function e^{bx} to double in size. ◄

An example of the exponential function is in the decay of radioactive isotopes. If N_0 is the number of atoms of the isotope at time $t = 0$, the number at any other time, t, is given by

$$N(t) = N_0 e^{-t/\tau}, \tag{1.21}$$

where τ is called the *relaxation time*. It is the time for the number of atoms of the isotope to drop to $1/e = 0.367879$ of its original value. The time that is required for the number of atoms to drop to half its original value is called the *half-time* or *half-life*, denoted by $t_{1/2}$.

EXAMPLE 1.2 Show that $t_{1/2}$ is equal to $\tau \ln(2)$.

SOLUTION ► If $t_{1/2}$ is the half-life, then

$$e^{-t_{1/2}/\tau} = \frac{1}{2}.$$

Thus

$$\frac{t_{1/2}}{\tau} = -\ln\left(\frac{1}{2}\right) = \ln(2). \tag{1.22}$$

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EXERCISE 1.8 ► A certain population is growing exponentially and doubles in size each 30 years.
(a) If the population includes 4.00×10^6 individuals at $t = 0$, write the formula giving the population after a number of years equal to t.
(b) Find the size of the population at $t = 150$ years. ◄

EXERCISE 1.9 ► A reactant in a first-order chemical reaction without back reaction has a concentration governed by the same formula as radioactive decay,

$$[A]_t = [A]_0 \, e^{-kt},$$

where $[A]_0$ is the concentration at time $t = 0$, $[A]_t$ is the concentration at time t, and k is a function of temperature called the rate constant. If $k = 0.123\ \text{s}^{-1}$, find the time required for the concentration to drop to 21.0% of its initial value. ◄

1.3 Units of Measurement

The measurement of a length or other variable would be impossible without a standard definition of the unit of measurement. For many years science and commerce were hampered by the lack of accurately defined units of measurement. This problem has been largely overcome by precise measurements and international agreements. The internationally accepted system of units of measurements is called the *Systéme International d'Unités*, abbreviated *SI*. This is an *MKS system*, which means that length is measured in meters, mass in kilograms, and time in seconds. In 1960 the international chemical community agreed to use SI units,

TABLE 1.2 ► SI Units

SI base units (units with independent definitions)

Physical quantity	**Name of unit**	**Symbol**	**Definition**
Length	meter	m	Length such that the speed of light is exactly $299{,}792{,}458\ \mathrm{m\,s^{-1}}$.
Mass	kilogram	kg	The mass of a platinum-iridium cylinder kept at the International Bureau of Weights and Measures in France.
Time	second	s	The duration of $9{,}192{,}631{,}770$ cycles of the radiation of a certain emission of the cesium atom.
Electric current	ampere	A	The magnitude of current which, when flowing in each of two long parallel wires 1 m apart in free space, results in a force of 2×10^7N per meter of length.
Temperature	kelvin	K	Absolute zero is 0 K; triple point of water is 273.16 K.
Luminous intensity	candela	cd	The luminous intensity, in the perpendicular intensity direction, of a surface of $1/600,\ 000\ \mathrm{m^2}$ of a black body at temperature of freezing platinum at a pressure of $101{,}325\ \mathrm{N\,m^{-2}}$.
Amount of substance	mole.	mol	Amount of substance that contains as many elementary units as there are carbon atoms in exactly 0.012 kg of the carbon-12 (^{12}C) isotope.

Other SI units (derived units)

Physical quantity	**Name of unit**	**Physical dimensions**	**Symbol**	**Definition**
Force	newton	$\mathrm{kg\,m\,s^{-2}}$	N	$1\ \mathrm{N} = 1\ \mathrm{kg\,m\,s^{-2}}$
Energy	joule	$\mathrm{kg\,m^2\,s^{-2}}$	J	$1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$
Electrical charge	coulomb	A s	C	$1\ \mathrm{C} = 1\ \mathrm{A\,s}$
Pressure	pascal	$\mathrm{N\,m^{-2}}$	Pa	$1\ \mathrm{Pa} = 1\ \mathrm{N\,m^{-2}}$
Magnetic field	tesla	$\mathrm{kg\,s^{-2}\,A^{-1}}$	T	$1\ \mathrm{T} = 1\ \mathrm{kg\,s^{-2}\,A^{-1}} = 1\ \mathrm{Wb\,m^{-2}}$
Luminous flux	lumen	cd sr	lm	$1\ \mathrm{lm} = 1\ \mathrm{cd\,sr}$ (sr = steradian)

which had been in use by physicists for some time.[5] The seven base units given in Table 1.2 form the heart of the system. The table also includes some derived units, which owe their definitions to the definitions of the seven base units.

Multiples and submultiples of SI units are commonly used.[6] Examples are the millimeter and kilometer. These multiples and submultiples are denoted by standard prefixes attached to the name of the unit, as listed in Table 1.3. The abbreviation for a multiple or submultiple is obtained by attaching the prefix abbreviation

[5] See "Policy for NBS Usage of SI Units," *J. Chem. Educ.* **48**, 569 (1971).

[6] There is a possibly apocryphal story about Robert A. Millikan, a Nobel-prize-winning physicist who was not noted for false modesty. A rival is supposed to have told Millikan that he had defined a new unit for the quantitative measure of conceit and had named the new unit the kan. However, 1 kan was an exceedingly large amount of conceit so for most purposes the practical unit was to be the millikan.

TABLE 1.3 ► Prefixes for Multiple and Submultiple Units

Multiple	Prefix	Abbreviation	Multiple	Prefix	Abbreviation
10^{12}	tera-	T	10^{-3}	milli-	m
10^{9}	giga-	G	10^{-6}	micro-	μ
10^{6}	mega-	M	10^{-9}	nano-	n
10^{3}	kilo-	k	10^{-12}	pico-	p
1	—	—	10^{-15}	femto-	f
10^{-1}	deci-	d	10^{-18}	atto-	a
10^{-2}	centi-	c			

to the unit abbreviation, as in Gm (gigameter) or ns (nanosecond). Note that since the base unit of length is the kilogram, the table would imply the use of things such as the mega kilogram. Double prefixes are not used. We use gigagram instead of megakilogram. The use of the prefixes for 10^{-1} and 10^{-2} is discouraged, but centimeters will probably not be abandoned for many years to come. The Celsius temperature scale also remains in common use among chemists.

Some non-SI units continue to be used, such as the *atmosphere* (atm), which is a pressure defined to equal $101,325\,\mathrm{N\,m^{-2}}$ ($101,325\,\mathrm{Pa}$), the *liter* (l), which is exactly $0.001\,\mathrm{m}^3$, and the *torr*, which is a pressure such that exactly 760 torr equals exactly 1 atm. The *Celsius temperature scale* is defined such that the degree Celsius (°C) is the same size as the kelvin, and 0 °C is equivalent to 273.15 K.

In the United States of America, English units of measurement are still in common use. The *inch* (in) has been redefined to equal exactly 0.0254 m. The *foot* (ft) is 12 inches and the mile (mi) is 5280 feet. The *pound* (lb) is equal to 0.4536 kg (not an exact definition; good to four significant digits).

Any measured quantity is not completely specified until its units are given. If a is a length equal to 10.345 m, one must write

$$a = 10.345\,\mathrm{m} \tag{1.23}$$

not just

$$a = 10.345 \quad \text{(not correct).}$$

It is permissible to write

$$a/\mathrm{m} = 10.345$$

which means that the length a divided by 1 m is 10.345, a dimensionless number. When constructing a table of values, it is convenient to label the columns or rows with such dimensionless quantities.

When you make numerical calculations, you should make certain that you use consistent units for all quantities. Otherwise, you will likely get the wrong answer. This means that (1) you must convert all multiple and submultiple units to the base unit, and (2) you cannot mix different systems of units. For example, you cannot correctly substitute a length in inches into a formula in which the other quantities are in SI units without converting. It is a good idea to write the unit as well as the number, as in Eq. (1.23), even for scratch calculations. This will help you avoid some kinds of mistakes by inspecting any equation and making sure that both sides are measured in the same units. In 1999 a U.S. space vehicle optimistically named the *Mars Climate Orbiter* crashed into the surface of Mars instead of orbiting the planet. The problem turned out to be that engineers working on the project had used English units such as feet and pounds, whereas physicists had used metric units such as meters and kilograms. A failure to convert units properly cost U.S. taxpayers several millions of dollars and the loss of a possibly useful mission. In another instance, when a Canadian airline switched from English units to metric units, a ground crew miscalculated the mass of fuel needed for a flight. The jet airplane ran out of fuel, but was able to glide to an unused military airfield and make a "deadstick" landing. Some people were having a picnic on the unused runway, but were able to get out of the way. There was even a movie made about the incident.

1.4 Numerical Calculations

The most common type of numerical calculation in a chemistry course is the calculation of one quantity from the numerical values of other quantities, guided by some formula. There can be familiar formulas that are used in everyday life and there can be formulas that are specific to chemistry. Some formulas require only the four basic arithmetic operations: addition, subtraction, multiplication, and division. Other formulas require the use of the exponential, logarithms, or trigonometric functions. The formula is a recipe for carrying out the specified numerical operations. Each quantity is represented by a symbol (a letter) and the operations are specified by symbols such as $\times$, $/$, $+$, $-$, ln, and so on. A simple example is the familiar formula for calculating the volume of a rectangular object as the product of its height (h), width (w), and length (l):

$$V = h \times w \times l$$

The symbol for multiplication is often omitted so that the formula would be written $v = hwl$. If two symbols are written side by side, it is understood that the quantities represented by the symbols are to be multiplied together. Another example is the *ideal gas equation*

$$P = \frac{nRT}{V} \tag{1.24}$$

where P represents the pressure of the gas, n is the amount of gas in moles, T is the absolute temperature, V is the volume, and R is a constant known as the *ideal gas constant*.

Significant Digits in a Calculated Quantity

When you calculate a numerical value that depends on a set of numerical values substituted into a formula, the accuracy of the result depends on the accuracy of the first set of values. The number of significant digits in the result depends on the numbers of significant digits in the first set of values. Any result containing insignificant digits must be rounded to the proper number of digits.

Multiplication and Division

There are several useful rules of thumb that allow you to determine the proper number of significant digits in the result of a calculation. For multiplication of two or more factors, the rule is that the product will have the same number of significant digits as the factor with the fewest significant digits. The same rule holds for division. In the following example we use the fact that the volume of a rectangular object is the product of its length times its width times its height.

EXAMPLE 1.3 What is the volume of a rectangular object whose length is given as 7.78 m, whose width is given as 3.486 m, and whose height is 1.367 m?

SOLUTION ▶ We denote the volume by V and obtain the volume by multiplication, using a calculator.

$$V = (7.78\,\mathrm{m})(3.486\,\mathrm{m})(1.367\,\mathrm{m}) = 37.07451636\,\mathrm{m}^3 = 37.1\,\mathrm{m}^3\ .$$

The calculator delivered 10 digits, but we round the volume to $37.1\,\mathrm{m}^3$, since the factor with the fewest significant digits has three significant digits. ◀

EXAMPLE 1.4 Compute the smallest and largest values that the volume in Example 1.1 might have and determine whether the answer given in Example 1.1 is correctly stated.

SOLUTION ▶ The smallest value that the length might have, assuming the given value to have only significant digits, is 7.775 m, and the largest value that it might have is 7.785 m. The smallest possible value for the width is 3.4855 m, and the largest value is 3.4865 m. The smallest possible value for the height is 1.3665 m, and the largest value is 1.3675 m. The minimum value for the volume is

$$V_{\mathrm{min}} = (7.775\,\mathrm{m})(3.4855\,\mathrm{m})(1.3665\,\mathrm{m}) = 37.0318254562\,\mathrm{m}^3\ .$$

The maximum value is

$$V_{\mathrm{max}} = (7.785\,\mathrm{m})(3.4865\,\mathrm{m})(1.3675\,\mathrm{m}) = 37.1172354188\,\mathrm{m}^3\ .$$

Obviously, all of the digits beyond the first three are insignificant. The rounded result of $37.1\,\mathrm{m}^3$ in Example 1.1 contains all of the digits that can justifiably be given. However, in this case there is some chance that $37.0\,\mathrm{m}^3$ might be closer to the actual volume than is $37.1\,\mathrm{m}^3$. We will still consider a digit to be significant if it might be incorrect by ± 1. ◀

Addition and Subtraction

The rule of thumb for significant digits in addition or subtraction is that for a digit to be significant, it must arise from a significant digit in every term of the sum or difference. You cannot simply count the number of significant digits in every term.

EXAMPLE 1.5 Determine the combined length of two objects, one of length 0.783 m and one of length 17.3184 m.

SOLUTION ▶ We make the addition:

$$\begin{array}{r} 0.783\,\mathrm{m} \\ 17.3184\,\mathrm{m} \\ \hline 18.1014\,\mathrm{m} \end{array} \quad \approx 18.101\,\mathrm{m}$$

The fourth digit after the decimal point in the sum could be significant only if that digit were significant in every term of the sum. The first number has only three significant digits after the decimal point. We must round the answer to 18.101 m. Even after this rounding, we have obtained a number with five significant digits, while one of our terms has only three significant digits. ◀

In a calculation with several steps, it is not a good idea to round off the insignificant digits at each step. This procedure can lead to accumulation of *round-off error*. A reasonable policy is to carry along at least one insignificant digit during the calculation, and then to round off the insignificant digits at the final answer. When using an electronic calculator, it is easy to use all of the digits carried by the calculator and then to round off at the end of the calculation.

Significant Digits in Trigonometric Functions, Logarithms, and Exponentials

If you are carrying out operations other than additions, subtractions, multiplications, and divisions, determining which digits are significant is not so easy. In many cases the number of significant digits in the result is roughly the same as the number of significant digits in the argument of the function, but more accurate rules of thumb can be found.[7] If you need an accurate determination of the number of significant digits when applying these functions, it might be necessary to do the operation with the smallest and the largest values that the number on which you must operate can have (incrementing and decrementing the number).

EXAMPLE 1.6 Calculate the following. Determine the correct number of significant digits by incrementing or decrementing.

(a) $\sin(372.15°)$ (b) $\ln(567.812)$

(c) $e^{-9.813}$.

SOLUTION ► (a) Using a calculator, we obtain

$$\begin{aligned} \sin(372.155°) &= 0.210557 \\ \sin(372.145°) &= 0.210386. \end{aligned}$$

Therefore,

$$\sin(372.15°) = 0.2105.$$

The value could be as small as 0.2104, but we write 0.2105, since we routinely declare a digit to be significant if it might be wrong by just ± 1. Even though the argument of the sine had five significant digits, the sine has only four significant digits.

(b) By use of a calculator, we obtain

$$\begin{aligned} \ln(567.8125) &= 6.341791259 \\ \ln(567.8115) &= 6.341789497. \end{aligned}$$

Therefore,

$$\ln(567.812) = 6.34179.$$

In this case, the logarithm has the same number of significant digits as its argument. If the argument of a logarithm is very large, the logarithm can have many more significant digits than its argument, since the logarithm of a large number is a slowly varying function of its argument.

[7] Donald E. Jones, "Significant Digits in Logarithm Antilogarithm Interconversions," *J. Chem. Educ.* **49**, 753 (1972).

(c) Using a calculator, we obtain

$$e^{-9.8135} = 0.00005470803$$
$$e^{-9.8125} = 0.00005476277.$$

Therefore, when we round off the insignificant digits,

$$e^{-9.8125} = 0.000547.$$

Although the argument of the exponential had four significant digits, the exponential has only three significant digits. The exponential function of fairly large arguments is a rapidly varying function, so fewer significant digits can be expected for large arguments. ◀

EXERCISE 1.10 ▶ Calculate the following to the proper numbers of significant digits.

(a) $(37.815 + 0.00435)(17.01 + 3.713)$

(b) $625[e^{12.1} + \sin(60.0\,°)]$

(c) 65.718×12.3

(d) $17.13 + 14.6751 + 3.123 + 7.654 - 8.123.$ ◀

The Factor-Label Method

This is an elementary method for the routine conversion of a quantity measured in one unit to the same quantity measured in another unit. The method consists of multiplying the quantity by a *conversion factor*, which is a fraction that is equal to unity in a physical sense, with the numerator and denominator equal to the same quantity expressed in different units. This does not change the quantity physically, but numerically expresses it in another unit, and so changes the number expressing the value of the quantity. For example, to express 3.00 km in terms of meters, one writes

$$(3.00\,\text{km})\left(\frac{1000\,\text{m}}{1\,\text{km}}\right) = 3000\,\text{m} = 3.00 \times 10^3\,\text{m}\,. \tag{1.25}$$

You can check the units by considering a given unit to "cancel" if it occurs in both the numerator and denominator. Thus, both sides of Eq. (1.25) have units of meters, because the km on the top cancels the km on the bottom of the left-hand side. In applying the method, you should write out the factors explicitly, including the units. You should carefully check that the unwanted units cancel. Only then should you proceed to the numerical calculation.

EXAMPLE 1.7 Express the speed of light, $2.9979 \times 10^8\ \text{m}\,\text{s}^{-1}$, in miles per hour. Use the definition of the inch, 1 in = 0.0254 m (exactly).

SOLUTION ▶

$$\left(2.9979 \times 10^8\,\text{m}\,\text{s}^{-1}\right)\left(\frac{1\,\text{in}}{0.0254\,\text{m}}\right)\left(\frac{1\,\text{ft}}{12\,\text{in}}\right)\left(\frac{1\,\text{mi}}{5280\,\text{ft}}\right)\left(\frac{60\,\text{s}}{1\,\text{min}}\right)\left(\frac{60\,\text{min}}{1\,\text{h}}\right)$$
$$= 6.7061 \times 10^8\,\text{mi}\,\text{h}^{-1}\,.$$

The conversion factors that correspond to exact definitions do not limit the number of significant digits. In this example, all of the conversion factors are exact definitions, so our answer has five significant digits because the stated speed has five significant digits. ◀

EXERCISE 1.11 ▶ Express the following in terms of SI base units. The electron volt (eV), a unit of energy, equals 1.6022×10^{-19} J.

(a) 24.17 mi
(b) $75\,\mathrm{mi\,h^{-1}}$
(c) $7.5\,\mathrm{nm\,ps^{-1}}$
(d) 13.6 eV

◀

SUMMARY

In this chapter, we introduced the use of numerical values and operations in chemistry. In order to use such values correctly, one must handle the units of measurement in which they are expressed. Techniques for doing this, including the factor-label method, were introduced. One must also recognize the uncertainties in experimentally measured quantities. In order to avoid implying a greater accuracy than actually exists, one must express calculated quantities with the proper number of significant digits. Basic rules for significant digits were presented.

PROBLEMS

1. Find the number of inches in a meter. How many significant digits could be given?

2. Find the number of meters in 1 mile and the number of miles in 1 kilometer, using the definition of the inch. How many significant digits could be given?

3. A furlong is one-eighth of a mile and a fortnight is 2 weeks. Find the speed of light in furlongs per fortnight, using the correct number of significant digits.

4. The distance by road from Memphis, Tennessee, to Nashville, Tennessee, is 206 miles. Express this distance in meters and in kilometers.

5. A U.S. gallon is defined as 231.00 cubic inches.

a) Find the number of liters in one gallon.

b) The volume of a mole of an ideal gas at 0.00 °C (273.15 K) and 1.000 atm is 22.414 liters. Express this volume in gallons and in cubic feet.

6. In the USA, footraces were once measured in yards and at one time, a time of 10.00 seconds for this distance was thought to be unattainable. The best runners now run 100 m in 10 seconds. Express 100 m in yards, assuming three significant digits. If a runner runs 100 m in 10.00 s, find his time for 100 yards, assuming a constant speed.

7. Find the average length of a century in seconds and in minutes, finding all possible significant digits. Use the fact that a year ending in 00 is not a leap year unless the year is divisible by 400, in which case it is a leap year. Find the number of minutes in a microcentury.

8. A light year is the distance traveled by light in one year.

a) Express this distance in meters and in kilometers. Use the average length of a year as described in the previous problem. How many significant digits can be given?

b) Express a light year in miles.

9. The *Rankine temperature scale* is defined so that the Rankine degree is the same size as the Fahrenheit degree, and 0 °R is the same as 0 K.

a) Find the Rankine temperature at 0.00 °C.

b) Find the Rankine temperature at 0.00 °F.

10. Calculate the mass of AgCI that can be precipitated from 10.00 ml of a solution of NaCl containing 0.345 mol l^{-1}. Report your answer to the correct number of digits.

11. The volume of a sphere is given by

$$V = \frac{4}{3}\pi r^3 \tag{1.26}$$

where V is the volume and r is the radius. If a certain sphere has a radius given as 0.005250 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the sphere might have with the given information and check your first answer for the volume.

12. The volume of a right circular cylinder is given by

$$V = \pi r^2 h,$$

where V is the volume, r is the radius, and h is the height. If a certain right circular cylinder has a radius given as 0.134 m and a height given as 0.318 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the cylinder might have with the given information and check your first answer for the volume.

13. The value of a certain angle is given as 31 °. Find the measure of the angle in radians. Using a table of trigonometric functions or a calculator, find the smallest and largest values that its sine and cosine might have and specify the sine and cosine to the appropriate number of digits.

14.

a) Some elementary chemistry textbooks give the value of R, the ideal gas constant, as 0.0821 l atm K^{-1} mol^{-1}. Using the SI value, 8.3145 J K^{-1} mol^{-1}, obtain the value in l atm K^{-1} mol^{-1} to five significant digits.

b) Calculate the pressure in atmospheres and in N m^{-2} (Pa) of a sample of an ideal gas with $n = 0.13678$ mol, $V = 1.000$ l and $T = 298.15$ K, using the value of the ideal gas constant in SI units.

c) Calculate the pressure in part b in atmospheres and in N m^{-2} (Pa) using the value of the ideal gas constant in l atm K^{-1} mol^{-1}.

15. The van der Waals equation of state gives better accuracy than the ideal gas equation of state. It is

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

where a and b are parameters that have different values for different gases and where $V_m = V/n$, the molar volume. For carbon dioxide, $a = 0.3640\,\mathrm{Pa\,m^6\,mol^{-2}}$, $b = 4.267 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$. Calculate the pressure of carbon dioxide in pascals, assuming that $n = 0.13678\,\mathrm{mol}$, $V = 1.000\,\mathrm{l}$, and $T = 298.15\,\mathrm{K}$. Convert your answer to atmospheres and torr.

16. The *specific heat capacity* (specific heat) of a substance is crudely defined as the amount of heat required to raise the temperature of unit mass of the substance by 1 degree Celsius (1 °C). The specific heat capacity of water is $4.18\,\mathrm{J\,°C^{-1}\,g^{-1}}$. Find the rise in temperature if 100.0 J of heat is transferred to 1.000 kg of water.